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中药茅莓化学成分研究

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摘 要：用溶剂提取和硅胶柱层析分离的方法，根据光谱分析鉴定中药茅莓的结构，分离并鉴定了 5 个化合物，分别为 β-谷甾醇(Ⅰ)、蔷薇酸(Ⅱ)、2α,3α,19α,23-tetrahydroxy urs-12-en-28-oic acid(Ⅲ)、β-葫萝卜甙(Ⅳ)和悬钩子皂甙(Ⅴ)，以上前四个化合物均为首次从该植物中分得。

关键词：茅莓；化学成分；三萜

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Studies on the chemical constituents from the Chinese traditional medicine *Rubus parvifolius*

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Abstract: To study the chemical constituents in *Rubus parvifolius*, chromatography and spectral analyses were used to isolate the constituents and elucidate of their structure. Five compounds were isolated and identified as: β-sitosterol(Ⅰ); euscaphic acid(Ⅱ); 2α, 3α, 19α, 23-tetrahydroxyurs-12-en-28-oic acid(Ⅲ); daucosteorl(Ⅳ); suavissimoside R_1(Ⅴ). The former four compounds were obtained from this plant for the first time.

Key words: *Rubus parvifolius*; constituents; triterpenoids

茅莓(*Rubus parvifolius* L.)为蔷薇科(Rosaceae)悬钩子属植物，落叶小灌木，生于山坡、路旁荒地、灌丛和草丛中，适应性强，资源十分丰富，分布于河北、山西、陕西、四川以及中南和华东各省(中国植物志委员会，1985)。茅莓根、茎、叶及全草均可药用，具有清热凉血、散结止痛、利尿消肿等功效，常用于治疗肠炎、肝脾肿大、黄疸、慢性肝炎、跌打肿痛、风湿骨痛、泌尿系统感染等(江苏新医学院，1997)。药理实验表明，茅莓的水提物具有止血和活血化瘀作用(朱志华等，1990)，并且与已成功用于治疗冠心病、心绞痛等多种心血管疾病的活血化瘀药物丹参的药理作用相同。但是关于茅莓化学成分的研究目前从该植物中只分出了 2 个三萜化合物(王先荣等，1994)。为了探索该植物的有效成分，进一步挖掘其药用潜能，更好地利用我区这一丰富资源，我们对茅莓的化学成分进行了研究，从其根部乙醇提取物中乙酸乙酯部位分离得到 5 个单体化合物，3 个是三萜化合物，结构鉴定为：β-谷甾醇(Ⅰ)、蔷薇酸

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(Ⅱ)、2α,3α,19α,23-tetrahydroxy urs-12-en-28-oic acid(Ⅲ)、β-葫萝卜甙(Ⅳ)和悬钩子皂甙(Ⅴ),以上前四个化合物均为首次从该植物中分得。

1 仪器与材料

X4型微量熔点测定仪(未校正),Perkin-Elmer 983G型IR光谱仪,VG20-253质谱仪,Varian-INOVA500MHz超导核磁共振波谱仪,薄层层析硅胶G、GF254和柱层析硅胶(100～200目)均为浙江雁荡山试剂厂产品。植物于2001年10月采自广西玉林市郊,经玉林师范学院化生系蒋波副教授鉴定为茅莓(*Rubus parvifolius* L)。

2 提取与分离

干燥的茅莓根2 kg,粉碎成粗粉,95%乙醇回流提取3次,合并提取液,减压蒸除溶剂后得到浸膏169 g。将浸膏分散于一定量热水中,振摇,使其悬浮于水中,依次用60～90 ℃石油醚、乙酸乙酯、水饱和正丁醇萃取,乙酸乙酯萃取物经硅胶(100～200目)柱层析分离,用氯仿：甲醇(20：1,10：1,5：1,1：1)梯度洗脱,每200 mL为一流份,共收集63份。TLC薄层检测后,合并相同部分,其中Fr11乙醇重结晶得白色针状晶体(Ⅰ),Fr12-Fr38合并为A,Fr47-Fr51合并为B;Fr52-Fr60合并为C。

将A再经反复硅胶柱层析分离,氯仿：甲醇(20：1～1：1)梯度洗脱得化合物Ⅱ,B经石油醚：丙酮(5：1～1：1)洗脱,反复硅胶柱层析分离,得化合物Ⅲ,C经硅胶柱层析分离,氯仿：甲醇(20：1～1：1)梯度洗脱,得化合物Ⅳ和Ⅴ。

3 结构鉴定

化合物Ⅰ:白色针状结晶(乙醇重结晶),mp:140～142 ℃。Libermann-Burchard反应呈阳性,薄层层析氯仿:石油醚(1：1)检查为单一斑点,Rf值为0.58,与β-谷甾醇文献值比较Rf值相符。$IR_{max}^{CHCl_3}$ cm^{-1}:3426,2936,1464,1056;^{1}HNMR($CDCl_3$)δ:0.68(3H,s,18-CH_3),1.01(3H,s,19-CH_3),0.92(3H,d,J=6.5Hz,21-CH_3),0.84(3H,d,J=8 Hz,29-CH_3),0.83(3H,d,J=5.5Hz,26-CH_3),0.81(3H,d,J=7.0 Hz,27-CH_3),3.52(brs,1H,3-H),5.53(brs,1H,6-H)。该化合物^{13}CNMR($CDCl_3$)数据(表1),上述波谱数据与文献(Kojima等,1990)报道的β-谷甾醇的数据吻合,所以鉴定该化合物为β-谷甾醇(β-sitosterol)。

化合物Ⅱ:白色针状结晶,mp:271～272 ℃,Libermann-Burchard反应呈阳性。在紫外灯下(254 nm)无荧光斑点,5%硫酸—乙醇溶液显蓝色。FAB-MS:m/z 459[M^+-2×H_2O+Li],m/z 413[M^+-HCOOH-2×H_2O+Li],m/z 397[M^+-HCOOH-3×H_2O+Li];^{13}CNMR($CDCl_3$+DMSO-d_6)数据(表1);DEPT显示:分子中存在7个甲基,8个亚甲基,7个次甲基和8个季碳;^{1}HNMR($CDCl_3$+DMSO-d_6)δ:0.88(3H,d,J=6.5Hz),5.28(1H,brs,H-12),3.9(H-2,ddd,J=11.5Hz,),3.3(H-3,d)。所以推测该结构为2α,3α,19α-trihydroxy urs-12-en-28-oic acid,与文献(Takashi等,1984)报道的化合物蔷薇酸(euscaphic acid)波谱数据吻合。结构见图1。

化合物Ⅲ:白色粉末,Libermann-Burchard,Molish反应均为阳性,在紫外灯下(254 nm)无荧光斑点,5%硫酸—乙醇溶液显蓝色。$IR_{max}^{CHCl_3}$ cm^{-1}:3428,2935,1690,1044;FAB-MS:m/z 527[M^++Na],m/z 469[M^+-2×H_2O+Na],m/z 409[M^+-HCOOH+H];^{13}CNMR($CDCl_3$+DMSO-d_6)数据(表1);DEPT显示:分子中存在6个甲基,9个亚甲基,7个次甲基和8个季碳;^{1}HNMR($CDCl_3$+DMSO-d_6)δ:0.74,0.77,1.02,1.19,1.28(each 3H,s,H-26,H-24,H-25,H-27,H-29),0.92(3H,d,J=6Hz,H-30),2.6(1H,brs,H-18),3.39,3.51(each 1H,d,J=11 Hz,H-23),5.34(1H,brs,H-12),3.86(1H,ddd,J=10.6,4.5,3 Hz,H-2),3.65(1H,d,J=3 Hz,H-3)。所以推测该结构为2α,3α,19α,23-tetrahydroxy urs-12-en-28-oic acid,与文献(Takashi等,1984)报道的化合物2α,3α,19α,23-tetrahydroxy urs-12-en-28-oic acid波谱数据吻合。结构见图1。

化合物Ⅳ:白色粉末,Libermann-Burchard反应呈阳性,浓硫酸-α萘酚反应呈紫红色,在紫外灯下(254 nm)无荧光斑点,5%硫酸－乙醇溶液显红色,以5% H_2SO_4水解,水溶液检出葡萄糖。^{1}HNMR($CDCl_3$+DMSO-d_6)δ:5.35(1H,glc,1'-H),3.8-4.30(6H,glc,2'-6'H),1.0(3H,s,19-H),0.92(d,J=6.5Hz,21-H),0.87(d,J=7Hz,

26-H),0.85(3H,t,J=7,29-H),0.82(3H,d,J=6.5Hz,27-H),0.64(3H,s,18-H);^{13}CNMR($CDCl_3$+DMSO-d_6)数据(表1),对照文献(Takashi等,1990)报道的β-葫萝卜甙波谱数据,鉴定该化合物为

表1 化合物的^{13}CNMR数据

Table 1 ^{13}CNMR data of compounds

No.	Ⅱ		Ⅲ		Ⅴ		No.	Ⅱ		Ⅲ		Ⅴ	
	δ	DEPT	δ	DEPT	δ	DEPT		δ	DEPT	δ	DEPT	δ	DEPT
1	41.2	CH_2	41.2	CH_2	47.3	CH_2	19	72.0	C	72.7	C	72.6	C
2	65.2	CH_2	65.8	CH	67.1	CH	20	40.9	CH	42.0	CH	41.2	CH
3	78.0	CH	77.8	CH	77.6	CH	21	27.7	CH_2	26.9	CH_2	25.8	CH_2
4	37.6	CH_2	41.0	C	53.0	C	22	37.0	CH_2	37.2	CH_2	36.5	CH_2
5	46.8	C	46.5	CH	50.9	CH	23	28.2	CH_3	70.5	CH_2	178.1	C
6	21.5	CH	17.6	CH_2	20.2	CH_2	24	23.0	CH_3	16.3	CH_3	13.7	CH_3
7	32.1	CH_2	32.4	CH_2	32.1	CH_2	25	15.8	CH_3	17.0	CH_3	16.7	CH_3
8	39.0	CH	40.8	C	39.0	C	26	16.3	CH_3	16.5	CH_3	16.8	CH_3
9	47.3	CH	47.0	CH	47.0	CH	27	25.6	CH_3	25.2	CH_3	23.8	CH_3
10	37.6	C	37.6	C	37.4	C	28	179.5	C	180.0	C	175.5	C
11	24.0	CH_2	23.3	CH_2	23.2	CH_2	29	27.7	CH_3	27.3	CH_3	26.4	CH_3
12	127.3	CH_2	128.1	CH	126.8	CH	30	15.8	CH_3	15.9	CH_3	16.3	CH_3
13	138.1	C	138.1	C	138.1	C	1'					94.0	CH
14	40.0	CH	40.9	C	42.4	C	2'					76.7	CH
15	29.0	CH_2	28.3	CH_2	28.0	CH_2	3'					79.0	CH
16	26.4	CH_2	25.8	CH_2	25.0	CH_2	4'					67.1	CH
17	46.8	C	46.0	C	47.0	C	5'					72.2	CH
18	52.7	CH	52.8	CH	53.1	CH	6'					60.6	CH_2

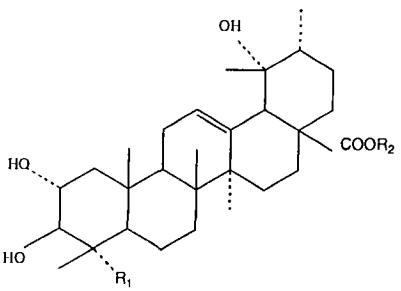

图1 化合物结构

Fig. 1 Structures of compounds

Ⅱ: R_1=H; R_2=H; Ⅲ: R_1=OH; R_2=H;
Ⅴ: R_1=COOH; R_2=glc.

β-葫萝卜甙(daucosteorl)。

化合物Ⅴ:白色针状结晶,Libermann-Burchard,Molish反应均为阳性,在紫外灯下(254 nm)无荧光斑点,5%硫酸-乙醇溶液显蓝色,薄层水解产生糖与标准品葡萄糖Rf值一致。$IR_{max}^{CHCl_3}$ cm^{-1}: 3412,2930,1729,1076;FAB-MS:m/z 519[M^+-glc+H],m/z 502[M^+-glc-H_2O+H],m/z 455[M^+-glc-HCOOH-H_2O+H],m/z 201,185,A系列离子碎片;($CDCl_3$+DMSO-d_6)数据(表1);DEPT显示:甙元分子中存在6个甲基,8个亚甲基,7个次甲基和9个季碳;^{1}HNMR($CDCl_3$+DMSO-d_6)δ:5.24(1H,dd,glc,1'-H),3.8-4.45(6H,glc,2'-6'H),5.2(1H,t,H-12),0.64,0.92,0.96,1.09,1.28(each 3H,s,H-26,H-24,H-25,H-27,H-29),0.84(3H,d,J=7Hz,H-30),2.5(1H,brs,H-18),4.60(1H,dd,J=10.5,4.5 Hz,H-2),3.07(1H,d,J=10 Hz,H-3)。所以推测该结构为28-β-glucopyranosyl ester of 2α,3β,19α-trihydroxy urs-12-en-23,28-dioic acid,与文献(Feng等,1985)报道的化合物28-β-glucopyranosyl ester of 2α,3β,19α-trihydroxy urs-12-en-23,28-dioic acid波谱数据吻合。结构见图1。

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flow in the respiratory action, which is in conform with the reinforcing of respiratory action and respiration can help the formation of phellogen around the wound. The quick wound healing of the plant can separate the healthy organization from the infectious parts so as to prevent infection spreading. The reinforcing of ascorbic acid oxidase activity is a sort of manifestation of the defending against pathogen infection of plant that is adapted to the enhancement of the respiratory action of diseased tissues. So a higher enzyme activity will result in a stronger disease resistance. From the above experimental results, it can be seen that *L. grandispicum* Y. J. Fei has quite strong disease resistance. And from the field observation, it was known that *L. grandispicum* Y. J. Fei do not have infectious status which is the same as actual measurement.

3 Discussion

The study reveals that *L. grandispicum* Y. J. Fei is highly resistant to aging and disease. The paper presented the preliminary study on *L. grandispicum* Y. J. Fei, but there are more issues waiting for further studies. For example, in the measurement of malondialdehyde content, only a certain time of malondialdehyde content was measured. In fact, for further study of degree of its resistance to aging, the malondialdehyde content should measured serially. Moreover, the extraction analysis of its isodynamic enzyme and DNA are still waiting for further studies.

In general, the preliminary study indicated that *L. grandispicum* Y. J. Fei is a sort of new germplasm resources. If the fine gene of *L. grandispicum* Y. J. Fei is transferred to wheat by the application of cell engineering, Chromosomal engineering and gene engineering, a genetic improvement of wheat is foreseeable.

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